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Hydrochloric Acid-Oxygen Leaching and Metal Recovery From a Copper-Nickel Bulk Sulfide Concentrate

By G. A. Smyres, K. P. V. Lei, and T. G. Carnahan

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES 75TH ANNIVERSARY

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UNITED STATES DEPARTMENT OF THE INTERIOR
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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mg/L	milligram per liter
ft/min	foot per minute	min	minute
ft^3/min	cubic foot per minute	mL	milliliter
g	gram	mV	millivolt
gal	gallon	oz	ounce
gal/(ft^2·h)	gallon per square foot per hour	tr oz/st	troy ounce per short ton
g/L	gram per liter	pct	percent
h	hour	psig	pound per square inch gauge
in	inch	r/min	revolution per minute
kg	kilogram	SCFM	standard cubic foot per minute
L	liter	st/d	short ton per day
L/kg	liter per kilogram	vol pct	volume percent
mg	milligram		

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HYDROCHLORIC ACID-OXYGEN LEACHING AND METAL RECOVERY FROM A COPPER-NICKEL BULK SULFIDE CONCENTRATE

By G. A. Smyres,[1] K. P. V. Lei,[2] and T. G. Carnahan[3]

ABSTRACT

The Bureau of Mines investigated a $HCl-O_2$ leaching procedure to recover Cu, Ni, and Co from a low-grade bulk sulfide flotation concentrate prepared from the Duluth gabbro complex. Since the Duluth gabbro complex is the largest known and unexploited Ni resource in the United States, the development of options for extracting the metal values from the flotation concentrate of this domestic resource is necessary. Conditions were determined for producing a pregnant solution low in Fe to facilitate recovery of the metal values. Leaching experiments were conducted at 15 pct solids, 100° to 120° C, 0.2 to 0.3 g HCl per gram concentrate in a 50-gal reactor pressurized to 50 psig with O_2. Base metal extractions from the concentrate were, in percent, 90 to 92 Cu, 99 Ni, 97 to 99 Co, and 0.1 Fe. Precious metals extractions were erratic and unpredictable; at best their extractions were, in percent, 55 Au, 90 Ag, 40 Pt, and 45 Pd. The reaction time at 120° C was 0.5 h. The use of compressed air instead of O_2 as the oxidant was also investigated. Solvent extraction using LIX 622 was used to remove Cu from the pregnant solution. Cementation on Cu was tested for precious metals recovery, while sulfide precipitation was used to produce a Ni-Co product. A conceptual flowsheet for treating the Duluth gabbro concentrate is proposed.

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INTRODUCTION

Major Cu-Ni deposits containing more than 4.4 billion st of material, which averages 0.66 pct Cu and 0.20 pct Ni (1),[4] occur along the northwestern basal contact of the Duluth gabbro complex in northeastern St. Louis and northwestern Lake Counties in Minnesota (fig. 1). This is the largest known Ni resource in the United States and is also a significant Cu resource. Associated with the Cu-Ni minerals are small amounts of Co and minor amounts of Ag, Au, Pt, and Pd. Because the resource represents a potential source of critical and strategic metals, the Bureau of Mines investigated the recovery of Cu, Ni, Co, and precious metals (PM's).

Recovery of two smelter feed concentrates, one high in Cu but low in Ni, and another high in Ni and low in Cu, would be the most desirable products from the resource, but current technology has not indicated the feasibility of this processing sequence. Since it has been demonstrated that a bulk flotation concentrate containing the Cu and Ni values (2-4) can be produced, the Bureau tested a number of extractive metallurgical techniques to recover the metals from the Cu-Ni concentrates. Methods investigated include sulfation roasting (5), matte smelting (6-7), physical beneficiation of mattes (8), and treatment of concentrates, mattes, and roasted mattes with H_2SO_4 or H_2SO_4 and O_2 (9-11).

Each approach has its problems. Sulfation roasting is temperature sensitive, and the temperatures necessary for high Cu and Ni extractions are different. Matte smelting emits SO_2 and recovers the following, in percent: 96 Cu, 85 Ni, but only 26 Co. Treatment of the slag from matte smelting by crushing, grinding, and sulfide flotation can increase these metal recoveries. Flotation of the matte produced two valuable products, a Cu-rich fraction that contained 90 pct of the Cu from the matte and a Ni-rich fraction that contained 87 pct of the Ni, 70 pct of the Co, and most of the Au, Pt, and Pd values from the matte. The Cu and Ni flotation products can be treated for metal recovery, but because losses at each step of processing are cumulative, final recoveries are low. Sulfuric acid leaching of concentrate, matte, or roasted matte dissolves more Fe (>50 pct) than is desirable and leaves considerable H_2SO_4 (>6 g/L) in the leaching solution when conditions are adjusted for >90 pct Cu and Ni extractions. The presence of Fe and excess H_2SO_4 in the pregnant solution complicates subsequent metal recoveries.

Autoclave leaching of Cu-Ni matte with H_2SO_4 and O_2 or air (10-11) extracted more than 95 pct of the Ni and Co from the matte. At final pH values greater than 1, 89 pct of the Fe remained in the leach residue. Recovery of the metals by this approach required two unit operations--matte smelting and leaching. Because of metal losses in each operation, the overall base-metal recoveries were lowered.

[4]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

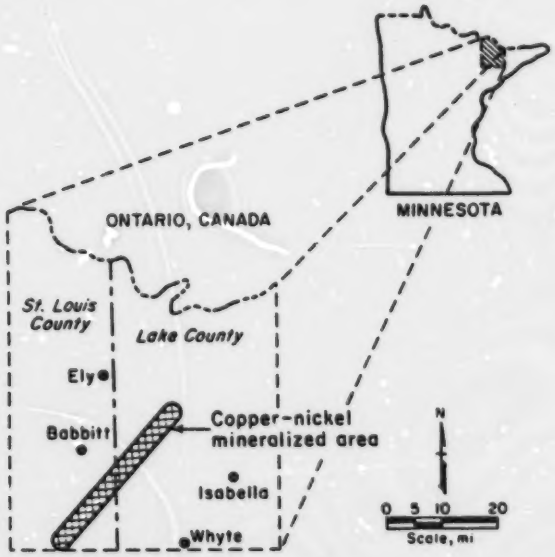

FIGURE 1. - Copper-nickel mineralized area of the Duluth gabbro complex, Minnesota.

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Prior Bureau research has shown that Cl^--O_2 hydrometallurgical procedures are effective for leaching base-metal sulfide concentrates (12-17). HCl and O_2 were used when HCl was expected to be produced from metal extraction operations, such as solvent extraction of Cu with oxime extractants (18). With this technique >99.9 pct of the Fe reports to the leach residue, and an almost Fe-free (<0.1 g/L) pregnant liquor is produced. Since the physical and chemical properties of the Duluth gabbro concentrate indicate that treatment by this technique could be successful, HCl-O_2 leaching was investigated as a possible extraction method.

LEACHING CHEMISTRY AND PROCESS CONSIDERATIONS

Analysis of the Duluth gabbro bulk sulfide concentrate is shown in table 1. The flotation concentrate was produced in a pilot plant. Principal sulfide minerals in the concentrate were pyrrhotite ($Fe_{1-x}S$), chalcopyrite ($CuFeS_2$), cubanite ($CuFe_2S_3$), and pentlandite ($(Fe,Ni)_9S_8$). The concentrate, when freshly produced, was 97 pct minus 200 mesh, but after prolonged storage, the fine particles cemented into >1-in lumps. The lumps were ground to minus 100 mesh for the small-scale leaching experiments; but, for the large-scale leaches, the concentrate was treated as received.

TABLE 1. - Analysis of Duluth gabbro copper-nickel bulk sulfide concentrate

Analysis, pct:	
Al	1.6
Cd, Pb and Zn	0.1
Co	0.093
Cu	9.3
Fe	28
Mg	0.88
Ni	1.6
S	1.0
S^{2-}	26.9
SO_4^{2-}	1.6
Analysis, tr oz/st:	
Ag	0.6
Au	0.013
Pt	0.016
Pd	0.034

Since the concentrate contained a large proportion of Fe-bearing sulfide minerals, leach conditions were sought that would minimize Fe dissolution, maximize Cu, Ni, and Co extractions, and simplify recovery of the metals from the pregnant solution. Dissolution of the metals occurs according to the following generalized leaching reaction:

$$MS + 2HCl + 1/2O_2 \rightarrow MCl_2 + S + H_2O \quad (1)$$

where MS denotes metal sulfides and MCl_2 represents metal chlorides. When the final pH is 1.4 to 2.0, coextracted Fe is oxidized and precipitated as goethite, FeO(OH), as shown by equation 2:

$$FeCl_2 + 1/4O_2 + 3/2H_2O \rightarrow FeO(OH) + 2HCl \quad (2)$$

The HCl from equation 2 reacts with base-metal sulfides according to equation 1. Also some S is oxidized to H_2SO_4 as shown by equation 3.

$$S + 3/2O_2 + H_2O \rightarrow H_2SO_4 \quad (3)$$

$CaCl_2$ is added to generate HCl and to remove sulfate from solution, as shown by equation 4:

$$H_2SO_4 + CaCl_2 \rightarrow 2HCl + CaSO_{4(s)} \quad (4)$$

HCl produced by reaction 4 also reacts with base-metal sulfides according to equation 1. These equations indicate that if the total amount of chloride in the reactor is sufficient to provide counter ions for all of the elements except Fe, an almost Fe-free base-metal pregnant solution can be obtained.

Since it has been reported that reaction rates for leaching sulfide minerals by oxidative systems increase with increasing temperature (19-20), the effect of temperature on the rate of HCl-O_2

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leaching of Duluth gabbro concentrate was one of the parameters investigated. Conversely, oxygen pressure does not influence the kinetics of oxidative systems in a chloride medium if sufficient O_2 is available during leaching (21). This seemingly indicates that leaching reactions can be sustained by the O_2 available in compressed air if proper gas-phase dispersion is provided within the reactor.

Recovery of Cu from the pregnant liquor can be accomplished by solvent extraction, cementation, sulfide or hydroxide precipitation, or hydrogen reduction. Solvent extraction was the method of choice because it yields a purified, aqueous, Cu-rich solution that is suitable for producing high-purity Cu (by electrowinning) as well as a HCl-bearing raffinate. This raffinate results from the exchange of H^+ for Cu^{2+} during organic loading and is recycled to the reactor for leaching concentrate.

Nickel and cobalt can be recovered from chloride solutions by precipitation as sulfides at pH 2 to 3 (22-24). $CaCO_3$ is used to adjust the pH of the solution and to replace the Ca lost from the system as $CaSO_4$. The (Ni,Co)S is suitable feed for existing Ni-Co refineries.

Precious metals can be leached also at a controlled potential in oxidizing chloride solutions (19). Conventional techniques for recovery of these metals were demonstrated, but exhaustive research on extraction and recovery was beyond the scope of this investigation. Waste water streams can be treated by conventional hydroxide-sulfide precipitation techniques (25-27) to prepare them for reuse or disposal.

A general description of the major steps in processing Duluth gabbro concentrate is shown in figure 2. Concentrate is leached with recycled HCl solution and O_2 to produce an almost Fe-free (<0.1 g Fe/L) solution containing Cu, Ni, Co, and PM's. After filtration, the pregnant solution is treated for PM recovery by cementation with Cu. Copper is removed by solvent extraction, and most of the raffinate is recycled to the leaching reactor, which causes the Ni-Co concentration in solution to build up. About 5 pct of the solvent extraction raffinate is bled and treated with $Ca(HS)_2$ at its natural pH to precipitate residual Cu as CuS. After Cu removal, the solution is treated again with $Ca(HS)_2$, at an adjusted pH of 2 to 3, to precipitate a (Ni,Co)S product. Sufficient Ni and Cu are thus extracted to maintain their concentrations in the recycle solution at a tolerable level.

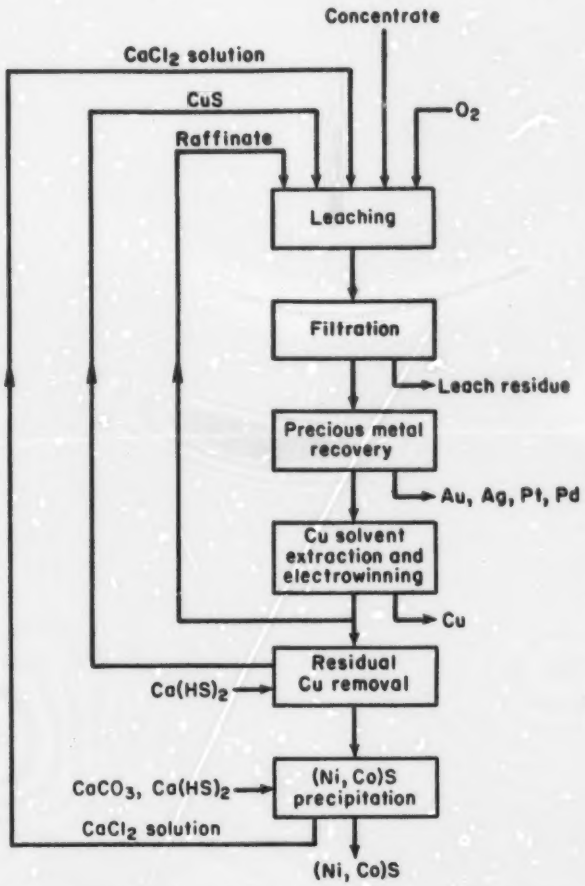

FIGURE 2. - Conceptual flow diagram for $HCl-O_2$ leaching.

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EQUIPMENT AND PROCEDURES

Preliminary leaching experiments were performed in a 0.5-L Parr[5] shaker-type hydrogenation apparatus. The rubber-stoppered glass reaction bottle was designed with inlets for a thermocouple well and a glass tube to admit O_2. It was pressure tested to 120 psig with a diaphragm-protected pressure gauge. Mixing of the slurry in the bottle was done by a rocking mechanism at a rate of 225 cycles per minute. Oxygen flow into the bottle was measured by a Hastings O_2 flowmeter-totalizer and was recorded as liters of O_2 consumed at standard temperature and pressure (STP). A heating mantle with a temperature controller was used to maintain a constant leaching temperature.

A typical charge to the small-scale leach reaction vessel consisted of 20 g concentrate, 100 mL water, and reagent-grade chemicals. After charging, the reactor was pressurized to 25 psig with O_2, and heating and rocking were started. When the reactor reached operating temperature, the pressure was increased to 50 psig. At a predetermined time interval, the reactor was cooled and the slurry was removed and filtered through a Buchner funnel. The filter cake was washed with 300 mL of distilled water. Pregnant liquor, wash water, and dried residue were analyzed.

After the small-scale leaching tests were successfully completed, larger scale leaching experiments were conducted in a 50-gal stirred reactor. Figure 3 is a schematic drawing of the reactor. The reactor vessel, a Pfaudler glass-coated steel kettle, was rated at 150 psig, jacketed for steam heating and water cooling, and fitted with a titanium lid equipped with a pressure rupture disc that is not shown in the drawing. A pH probe,[6] capable of operating at temperatures up to 120° C and pressures up to 80 psig, was used to monitor the pH during leaching. When operating with O_2, the gas flow was monitored through a Hastings mass flow meter. A flushing valve was provided at the bottom of the reactor to facilitate discharge of the slurry. Agitation and intense aeration were provided by a flat-bladed, 8-in-diam impeller and a draft tube assembly. Adequate aeration was achieved at 450 r/min, which gave an impeller tip speed of 940 ft/min. The agitation assembly was similar to the aeration mechanism of a flotation machine and is shown in figure 4. Gas is pulled into the impeller, where shearing action against a baffle housing ensures good gas-to-pulp contact.

Experiments in the 50-gal reactor were also conducted with compressed air. Since only the O_2 in the air is consumed by the chemical reactions, N_2 builds up in the vessel and a gas flow-through system must be used to release the N_2. A modification to the 50-gal reactor for operating with compressed air is shown in figure 5. Air pressure was controlled by using an offgas pressure regulator installed on the reactor lid. Compressed air flowed through an in-line air filter and a pressure regulator into the reactor airspace above the pulp. As the compressed air entered the chamber, it

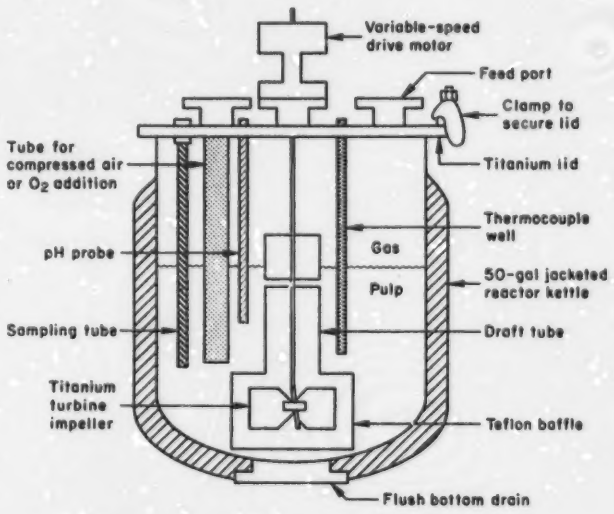

FIGURE 3. - Schematic view of 50-gal leaching reactor.

[5]Reference to specific products does not imply endorsement by the Bureau of Mines.

[6]Horiba Industrial pH Meter, Model K-7, made by Horiba Instruments Inc.

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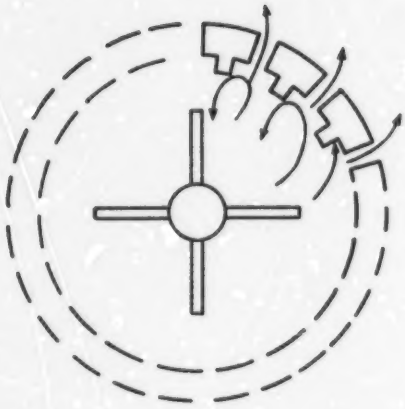

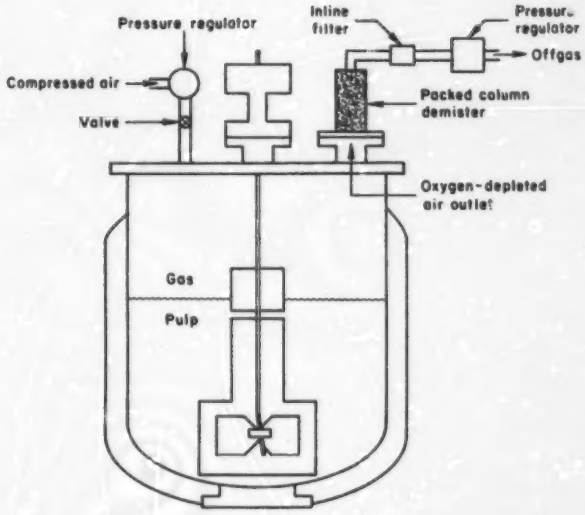

FIGURE 5. - Schematic configuration for leaching with HCl and compressed air.

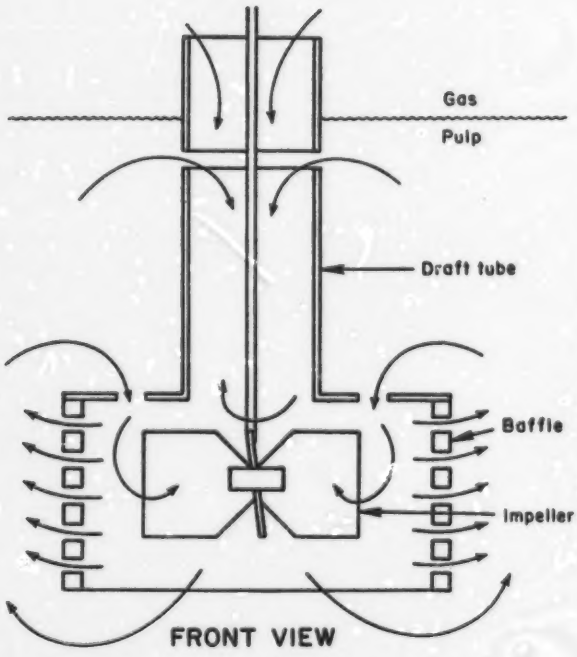

FIGURE 4. - Gas-pulp flow schematic for draft tube mixing.

combined with some of the reacted and O_2-depleted air already present in the reactor to form a mixture that was pulled into the pulp by the aeration system. Oxygen-depleted air exited through a column packed with 1/2-in ceramic saddles, to scavenge entrained liquid which was returned to the reactor, and then passed through an in-line pressure filter and the offgas pressure regulator.

Twenty kilograms of concentrate and 110 L of leaching solution were charged into the reactor to yield pregnant solution containing approximately 20 g/L Cu. The amount of HCl added to the reactor was less than that in the preliminary 0.5-L tests because of the greater amount of sulfate expected to be generated in this more intensely aerated reactor. The steam-jacketed reactor and charge were sealed, heated to the operating temperature, and pressurized to 50 psig with O_2. When operating the 50-gal reactor using O_2, the reaction was considered complete when the O_2 flow, which was initially very fast, had dropped to 0.08 SCFM. Monitoring the pH was the method used for determining completion of the test during operation of the 50-gal reactor while using compressed air. The reaction was considered complete when the pH value became constant. The reactor was cooled to 80° C, and the slurry was discharged from it. A sample of the slurry was filtered and washed, and the filtrate, wash water, and leach residue were analyzed. The procedure for operating with compressed air was the same as with O_2, except that gases were bled from the reactor at 2 to 5 ft^3/min during leaching, so that O_2 was always present in the reactor atmosphere.

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The O_2 content of the air bleed was not determined.

Cementation procedures were investigated to recover the PM's from a simulated pregnant solution. Cementation of Au, Ag, Pt, and Pd was conducted in a beaker at ambient temperature and with reactor filtrate spiked with Au, Ag, Pt, and Pd chlorides. Spiking provided higher concentrations of PM's in the leaching solution, which facilitated more accurate analyses for these metals. Five milligrams of Cu powder was added to 100 mL of solution, agitated for 1 h, and filtered. The solutions before and after treatment were analyzed.

Following the recovery of PM's, batch shaker and continuous mixer-settler tests were performed to study Cu recovery by solvent extraction with 15-pct LIX 622 in Escaid 200. The batch tests were conducted in 250-mL separatory funnels at organic-to-aqueous (O-A) ratios between 0.1 and 10 and at a contact time of 3 min to provide data for the equilibrium diagrams needed to design the mixer-settler circuit. Mixer-settler extraction experiments were conducted in equipment manufactured by Bell Engineering. Each mixer and settler had a volume of 175 and 385 mL, respectively. O-A ratios were 4 for loading, 5 for scrubbing, and 3 for stripping. Average residence time was 1.6 min in mixers and 3.3 min in settlers for loading stages; 1.7 min in mixers and 3.4 min in settlers for scrubbing stages; and 1.5 min in mixers and 3.1 min in settlers for stripping stages.

After solvent extraction of Cu, the raffinate was treated with controlled additions of $Ca(HS)_2$ to selectively precipitate residual copper as CuS, and nickel and cobalt as (Ni,Co)S. $Ca(HS)_2$ was produced by treating CaS with dilute H_2SO_4, as indicated by

$$2CaS + H_2SO_4 + 2H_2O \rightarrow Ca(HS)_2 + CaSO_4 \cdot 2H_2O \quad (5)$$

Completeness of precipitation and quantities of sulfide reagent required were determined by monitoring redox potentials of the solutions with a platinum electrode referenced to a Ag-AgCl electrode. For CuS precipitation, $Ca(HS)_2$ was added until the solution redox potential decreased to 50 mV. The pulp was filtered, and the CuS precipitate was washed, dried, and analyzed. To precipitate (Ni,Co)S, $CaCO_3$ and $Ca(HS)_2$ were added to the filtrate to maintain a pH of 2 to 3. Sulfide addition was stopped when the redox potential decreased to less than -400 mV. The pulp was filtered, and the precipitate was washed, dried, and analyzed.

Techniques used for making analytical determinations included inductively coupled plasma for metals in liquids and solids, atomic absorption for metals in organics, and wet chemical analysis for chloride and sulfur.

RESULTS AND DISCUSSION

LEACHING

Since solvent extraction of Cu produces acid that is recycled to the leaching reactor in the raffinate, preliminary experiments were performed at 110° C in the 0.5-L bottle reactor to determine the effect of HCl concentration in the raffinate on leaching. The independent variable was the concentration of HCl initially present in the chloride leaching solution. A synthetic solution was employed which contained, in grams per liter, 0.6 Cu, 45 Ni, 0.3 Co, 2.5 Ca, and 2.0 SO_4^{2-}. Composition of the solution was selected to simulate the projected recycle solution to the leaching reactor. Figure 6 shows that Cu extraction increased as initial HCl-concentrate ratios increased, but the Fe content of the leaching liquor also increased due to less hydrolysis, especially when the initial HCl-concentrate ratio was greater than 0.40. The data showed that a HCl-concentrate ratio which produced a pregnant solution with a terminal pH in the range of 1.7 to 1.8 extracted nearly 94 pct Cu and contained <0.1 g/L Fe. Other data from

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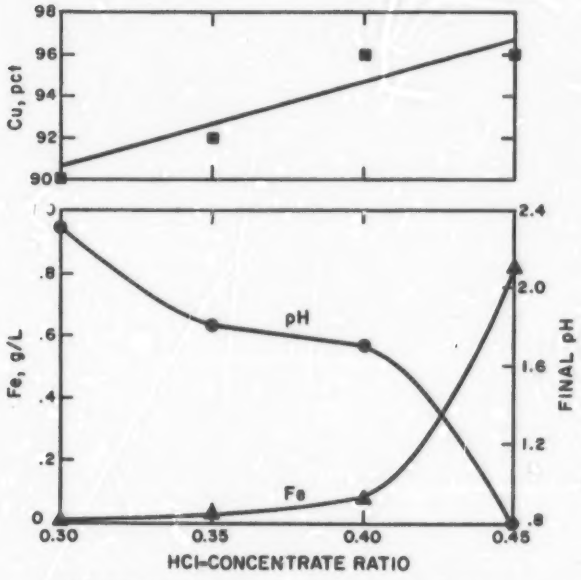

FIGURE 6. - Copper and iron extraction as functions of initial HCl concentration.

these experiments showed that extractions for Co and Ni were 98 to 99 pct and conversion of S to SO_4^{2-} was 10 pct. A total of 2.7 g/L Ca would be required to precipitate this sulfate as anhydrite ($CaSO_4$).

Additional leaching experiments were performed with the 50-gal reactor to determine the effect of temperature on the rate of reaction under more intense aeration than was possible in the bottle reactor, and to provide pregnant solution for solvent extraction experiments. Each test was pressurized to 50 psig with O_2 and used 20 kg of concentrate and 110 L of simulated chloride recycle solution which contained, in grams per liter, 45 Ni, 0.6 Cu, 0.3 Co, 5.6 Ca, 4.4 Mg, 2.0 SO_4^{2-}, and variable HCl amounts. Note the difference in Ca and Mg concentrations between this solution and the one used in the 0.5-L tests. The increased Ca concentration from these tests was necessary to control the anticipated greater percentage of SO_4^{2-} produced in the more intensely agitated slurry in the 50-gal reactor. Magnesium was added because the 0.5-L experiments yielded a pregnant liquor that contained the above level (4.4 g/L). An equilibrium concentration of Mg in solution would be obtained because water entrapped in the washed residue filter cake would act as a bleed stream for Mg. Moreover, $MgCl_2$ does not interfere with procedures for metal recovery from solution. Because temperature was the primary variable, the initial experiments in the 50-gal reactor were conducted to determine the influence at 100°, 105°, and 120° C. Extractions were 90 to 92 pct for Cu, 99 pct for Ni, and 97 to 99 pct for Co.

For maximum Cu recovery, adjustment of the pregnant solution's pH to almost 1.7 was made on hot pulps at the end of the leaching cycle. The initial HCl concentration was 80 pct of stoichiometric for experiments at 100° and 120° C and 53 pct of stoichiometric for the 105° C experiment. After leaching, slurries treated at 100° and 105° C had pH values higher than the desired 1.7. HCl was added in an attempt to obtain pH 1.7, but minimum values of 1.8 for 100° C and 2.0 for 105° C were attained. Concentrate slurried at 120° C was leached with excess HCl and had a final pH of 0.9. Table 2 shows the operating data for three 50-gal reactor tests and the final pH values after attempts to adjust the pH to 1.7.

TABLE 2. - Operating data for leaching concentrate in the 50-gal reactor at 50 psig O_2

	Leaching temperature		
	100° C	105° C	120° C
HCl-conc ratio:			
Initial.....	0.270	0.186	0.285
Total.....	0.305	0.237	0.285
O_2 consumed at STP....L/kg conc..	62.3	93.5	92.0
Reaction time...h..	5.5	2.0	0.5
Final pH.....	1.8	2.0	0.9
Fe.....g/L..	0.1	<0.01	2.0

Data in table 2 indicate that the time required for complete reaction decreased with increasing temperature. This temperature dependence of reaction time is consistent with the Arrhenius law. These results indicate that aeration in the 50-gal reactor was sufficient and did not control the rate of leaching.

The high Ni-Co and low Fe extractions corroborated results of tests conducted

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in the 0.5-L reactor. In experiments conducted at 100° and 105° C, the amount of HCl initially present was such that part of the Cu, which was converted from its original mineral form, was hydrolyzed to insoluble atacamite, $Cu_2(OH)_3Cl$. Most of the atacamite dissolved after the pH was adjusted to the 1.7 to 2.0 range by addition of HCl. The atacamite precipitation reaction presumed to occur during leaching is

$$12CuCl + 3O_2 + 6H_2O \rightarrow 4CuCl_2 + 4Cu_2(OH)_3Cl_{(s)} \quad (6)$$

Adding HCl after the conclusion of leaching dissolved the atacamite precipitate as follows:

$$Cu_2(OH)_3Cl_{(s)} + 3HCl \rightarrow 2CuCl_{2(aq)} + 3H_2O \quad (7)$$

In the experiment conducted at 120° C, enough HCl was present so that atacamite did not form.

The varying amount of SO_4^{2-} formed as temperature increased, and the resulting variations in Cu and Fe in solution due to hydrolysis reactions made it impossible to produce final leach slurries with the same pH, Fe, and Cu concentrations in the three 50-gal reactor tests at varying temperature. To compare results of these three tests, corrections to the total amount of HCl required in table 2 were calculated by normalizing the results of each experiment to an end pH of 1.8, Cu extraction of 92 pct, and with <0.1 g/L Fe. Table 3 shows the result. A smaller amount of total HCl was needed to obtain the final pH when leaching temperature was higher. Leaching at higher temperature or for longer duration produced H_2SO_4 by oxidation of sulfur and partly offset the need for additional HCl. This interpretation is supported by the observation that in the 105° and 120° C experiments, 14 to 15 pct of the sulfur was oxidized to SO_4, whereas in the 100° C experiment, only 12 pct was oxidized.

Precious metals extractions were erratic and not reproducible. The best estimates for extractions were, in percent, 55 Au, 90 Ag, 45 Pd, and 40 Pt.

TABLE 3. - Calculated total HCl requirement[1]

Temp:	
100° C	0.316
105° C	.239
120° C	.242

[1]Grams HCl per gram concentrate.

Oxygen cost is a major economic factor in hydrometallurgical processing of sulfide concentrates; this cost, however, can be decreased by substituting compressed air. The effect of using compressed air instead of O_2 was determined in the 50-gal reactor. The leaching conditions were 100° C, 55 psig, 0.28 g HCl per gram concentrate, and 4 h. The final pH of the slurry was adjusted from 2.8 to 1.8 by adding 0.01 g HCl per gram concentrate. Extractions of Cu, Ni, and Co were 86, 99, and 98 pct, respectively. Extraction of Fe was <0.1 pct. Water loss in air bleed was <0.1 L. The results demonstrate that compressed air was effective in the leaching. Decreasing leaching time would be expected if the leaching was conducted at temperature higher than 100° C. Increasing the acid in the leaching or postleaching pH adjustment would increase the copper extraction.

LIQUID-SOLID SEPARATION

Filtering rates were determined on 500-mL samples of 16-pct-solids pulp from tests conducted at 100° and 120° C. The slurry produced at 120° C was filtered at 60° C and 20-in-Hg vacuum. A cake thickness of 0.25 in and filtration rate of 5.7 gal/(ft^2·h) for the liquid and 7.7 lb/(ft^2·h) for the solid were obtained. Thirty milliliters of water was used for each displacement wash. Pulp produced by leaching at 120° C filtered twice as fast as pulp produced by leaching at 100° C. Elemental S, which melts at 119° C, probably caused the filtration rate difference, because at 100° C the S is finely divided and impeded filtration, but at 120° C the S agglomerated and formed larger particles that acted as a filter

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TABLE 4. - Displacement washing data on residue from 120° C test, grams per liter

Wash	Cu	Ni	Co	Fe	Ca	Mg	Cl
Filtrate....	23	59	0.66	0.10	11.0	6.3	95.9
1.....	19	53	.57	.04	4.0	5.4	NA
2.....	9.0	24	.26	.02	4.9	2.9	14.5
3.....	2.2	5.7	.06	.01	2.3	.66	NA
4.....	.75	1.89	.01	<.01	1.3	.20	NA
5.....	.28	.59	.00	<.01	.83	.08	3.1

NA Not analyzed.

aid. The moisture content of the 120° C leach residue was determined when the filtration cycle yielded cracking of the cake. A moisture content of 24 pct was measured by drying the cake at 80° C for 24 h.

Washing data for five successive displacements are given in table 4 for the 120° C reacted pulp. At least five washes were necessary to separate more than 99 pct of the soluble metal values from the residue. To prevent pollution by soluble base-metal chlorides leaching from discarded residue, the entrained base metals can be converted to insoluble sulfides by repulping with water and adding $Ca(HS)_2$.

METAL RECOVERY

Precious Metals Recovery

The results of a copper powder cementation test conducted on reactor filtrate augmented with Au, Ag, Pt, and Pd are shown in table 5. Cementation reduced the PM concentrations by >89 pct. The cementation product would be further processed into the individual metals at a PM refinery.

TABLE 5. - Recovery of Au, Ag, Pt, and Pd by cementation on Cu powder

Metal	Solution conc, mg/L		Recovery, pct
	Pregnant	Spent	
Au.....	35	<2	>94
Ag.....	48	5.1	89
Pt.....	100	<7	>93
Pd.....	130	<10	>93

Copper Recovery

Copper in pregnant solution containing, in grams per liter, Cu 23, Ni 59, Co 0.66, Fe 0.01, and Cl^- 124 was extracted with 15 vol pct LIX 622 in Escaid 200. The aqueous composition was a compromise between the desire to leach at high pulp solids content for minimizing reactor size, and to prevent high Cu concentrations in the solvent extraction raffinate. Strip liquor containing 31 g/L Cu and 122 g/L H_2SO_4 was produced for use as electrolyte for electrowinning (28). Results of batch tests indicated that four countercurrent extraction stages and four stripping stages were necessary to obtain approximately 8 g/L Cu in the raffinate. Two scrubbing stages were added to remove small amounts of entrained Ni and Cl^- from the loaded organic, which was subsequently stripped with a solution containing 18 g/L Cu and 150 g/L H_2SO_4.

A flowsheet for solvent extraction is shown in figure 7, and the analyses of process streams in the solvent extraction circuit are shown in table 6. The results show a small amount of Ni (148 mg/L) was coextracted with Cu in the first loading stage. However, as more Cu was loaded, Ni was released, as indicated by the composition of stream O_3. The feed contained no free acid, but acidity of the final raffinate was 1N due to exchange of H^+ for Cu^{2+}. Of the Cu in the pregnant solution, 65 pct was extracted by the solvent extraction step, and the remaining 35 pct was recycled to the reactor in the raffinate and as CuS.

The solvent extraction procedure produced a Cu solution that was suitable,

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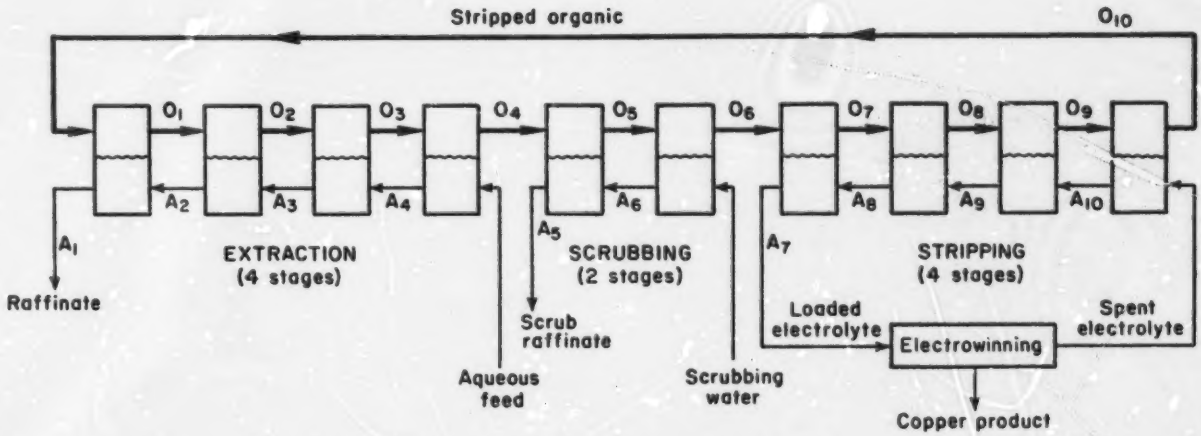

FIGURE 7. - Flowsheet for solvent extraction.

Table 6. - Composition of contents of mixer-settler stages

	Concentration, g/L				
	Cu	Ni	Co	Fe	Cl^-
AQUEOUS SOLUTION					
A_1	8	59	0.660	0.011	124
A_2	10	59	.660	.012	124
A_3	13	59	.660	.012	124
A_4	17	59	.660	.012	124
Aqueous feed	23	59	.660	.013	124
A_5	.046	.308	.0057	.0024	.009
A_6	.041	.280	.0047	.0024	.007
Spent electrolyte	18	<.003	<.001	<.0007	.004
A_7	31	.0080	.0015	<.0007	.170
A_8	26	.0069	.0015	<.0007	.015
A_9	23	<.003	.0014	<.0007	.009
A_{10}	19	<.003	.0014	<.0007	.007
ORGANIC SOLUTION					
O_1	3.8	0.148	<0.004	<0.004	<0.05
O_2	4.7	.067	<.004	<.004	<.05
O_3	6.0	<.004	<.004	<.004	<.05
O_4	7.3	<.004	<.004	<.004	<.05
O_5	7.3	<.004	<.004	<.004	<.05
O_6	7.3	<.004	<.004	<.004	<.05
O_7	6.3	<.004	<.004	<.004	<.05
O_8	4.9	<.004	<.004	<.004	<.05
O_9	4.1	<.004	<.004	<.004	<.05
O_{10}	3.4	<.004	<.004	<.004	<.05

except for chloride concentration, as Cu electrowinning feed. Generally, copper dendrites form on the copper plate during electrowinning if the Cl^- concentration of the electrolyte is >50 mg/L Cl^- (28). Although no Cl^- was detected in the organic, the Cl^- content of the $CuSO_4$-H_2SO_4 strip liquor still increased from 4 to 170 mg/L after four stripping and two washing stages. If necessary, the Cl^-

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concentration can be decreased by digesting powdered Cu in the strip solution for 1 h at 25° C to form insoluble CuCl, which can be filtered from the stripping solution. A laboratory test using this technique on the $CuSO_4$-H_2SO_4 strip liquor reduced the Cl^- content to 20 mg/L. The small amount of Ni transferred to the stripping solution (A_7) was codeposited with the Cu during electrolysis. This was not enough Ni to decrease the purity of the cathodes to <99.90 pct Cu.

Nickel-Cobalt Sulfide Precipitation

Copper remaining in the raffinate treated for Ni-Co recovery must be removed to prevent contamination of the (Ni,Co)S product. The residual Cu was precipitated as CuS with $Ca(HS)_2$. By carefully controlling the redox potential, formation of the H_2S was minimized. According to Burnham and Sumner (29), a solution redox potential of 50 to 100 mV corresponds to stoichiometric H_2S utilization in precipitating CuS from an acid sulfate solution. Figure 8 shows the redox potential of a solvent extraction raffinate solution during precipitation of CuS with $Ca(HS)_2$. The raffinate contained, in grams per liter, 9.1 Cu, 57 Ni, 0.7 Co, and 0.01 Fe. The $Ca(HS)_2$ solution contained 33 g/L S^{2-}. Complete Cu recovery was achieved when the redox potential of the slurry was <50 mV. The sulfide precipitate contained, in percent, 55 Cu, 4.9 Ni, 30 S, <0.03 combined Co, Cd, Pb, and Zn, and the balance $CaSO_4 \cdot 2H_2O$. No H_2S odor was detected from the filtrate or filter cake.

A combined (Ni,Co)S precipitate is suitable refinery feed. Thus, Ni and Co were recovered as mixed metal sulfides by $Ca(HS)_2$ precipitation from the Cu-free raffinate. The raffinate pH was increased to 3 with $CaCO_3$, and maintained between 2 and 3 during precipitation. Figure 9 shows the change in redox potential on addition of $Ca(HS)_2$ solution containing 67 g/L S^{2-}. The precipitation step for (Ni,Co)S was considered to be complete when the redox potential was less than -400 mV, which corresponded to a stoichiometric addition of sulfide (fig. 9). Since Cd, Pb, and Zn precipitate with Ni and Co, buildup of these metals in solution is also prevented. The (Ni,Co)S product contained, in percent, 43 Ni, 0.54 Co, 21 S, and <0.07 combined Cu, Cd, Pb, Zn, and Fe. More than 98 pct of the Ni and Co were recovered.

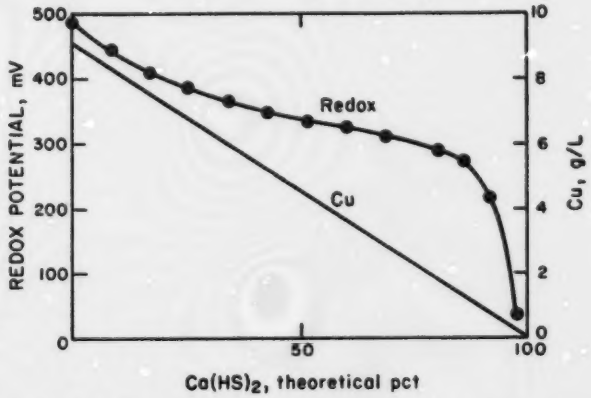

FIGURE 8. - Oxidation-reduction potential and copper in solution as a function of theoretical $Ca(HS)_2$ added for CuS precipitation.

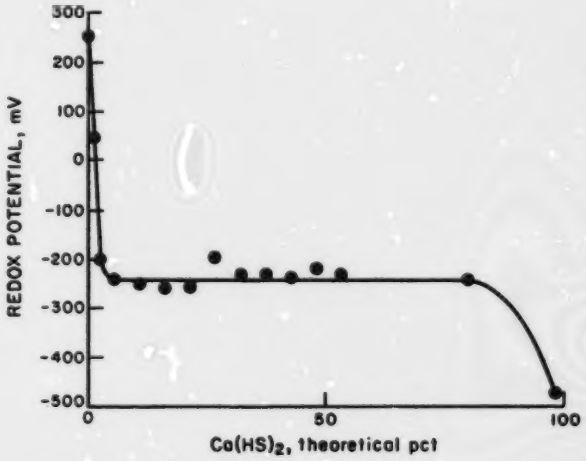

FIGURE 9. - Oxidation-reduction potential as a function of theoretical $Ca(HS)_2$ added for (Ni,Co)S precipitation.

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TREATMENT OF WASHING WATER

Washing water from the leach residue filtration step contained, in grams per liter, 5.8 Cu, 14 Ni, 0.2 Co, 3.9 Ca, and 11.8 Cl^-. Current hydroxide-sulfide waste water treatment technology (25-27) was used to make the water suitable for recycle. This involved increasing the pH to near 6 with lime or limestone to precipitate most of the metals as hydroxides, and then precipitating the remaining metals with sulfide. Analysis of the effluent after treatment is shown in table 7.

TABLE 7. - Analysis of washing water before and after treatment

Metal	Concentration, g/L	
	Before	After
Cu.....	5.8	<0.005
Ni.....	14.	.092
Co.....	.2	<.0012
Ca.....	3.9	13

The water treatment effluent would be used for recycle to the reactor and for the initial washing of reactor residue. Fresh water would be used for the final washing of the reactor residue and (Ni,Co)S precipitate. The amount of fresh water that can be used would equal the difference between water removed from the process in the washed residue and water coming into the process with the flotation concentrate.

ECONOMIC AND TECHNICAL EVALUATION

A preliminary economic and technical evaluation for a 1,000-st/d plant to treat bulk sulfide concentrate by the $HCl-O_2$ technique was prepared by the Bureau's Process Evaluation Group. The estimated operating cost of the proposed process is about $120/st concentrate, without including a charge for the flotation concentrate. Modifications designed to decrease capital and process costs should be concentrated on the leaching slurry filtration step, which accounted for 50 pct of the process plant capital cost and requires large amounts of water to wash the filter cake. Further research should be conducted on the solvent extraction circuit where considerable Cu remains in the raffinate.

PROPOSED FLOWSHEET

The $HCl-O_2$ leaching procedure produces high extractions of Cu, Ni, and Co and low extraction of Fe from Duluth gabbro concentrate. A proposed flowsheet using compressed air oxidant is shown in figure 10, and a material balance for a 1,000-st/d plant is shown in table 8. The numbers on the flow lines in figure 10 correspond to the streams in table 8. The concentrate is leached with HCl and compressed air. Leaching reactions convert the concentrate's sulfide minerals into metal chlorides and S. Iron in the concentrate forms insoluble iron oxides and reports to the tailings with the S and $CaSO_4$. Coextracted PM's are recovered from the pregnant solution by cementation using Cu. Copper is recovered from PM-free solution by solvent extraction to produce a Cu-bearing electrolyte for electrowinning. Of the acidic raffinate from the solvent extraction circuit, 95 pct is recycled to the reactor. $CaCl_2$ is added to the reactor to make up for chloride lost to the washed leach residue. H_2SO_4 is used as the acid makeup; it reacts with $CaCl_2$ to form HCl and $CaSO_4$.

Copper raffinate withdrawn for Ni and Co recovery is purified by removing Cu by sulfide precipitation. The pH of the filtrate after Cu removal is adjusted with $CaCO_3$ to allow precipitation of Ni and Co as sulfides. Wash water generated from different unit operations is treated to decrease its load of dissolved metals. Of the treated water, 95 pct is reused for residue washing, while 5 pct is recycled to the reactor as makeup water.

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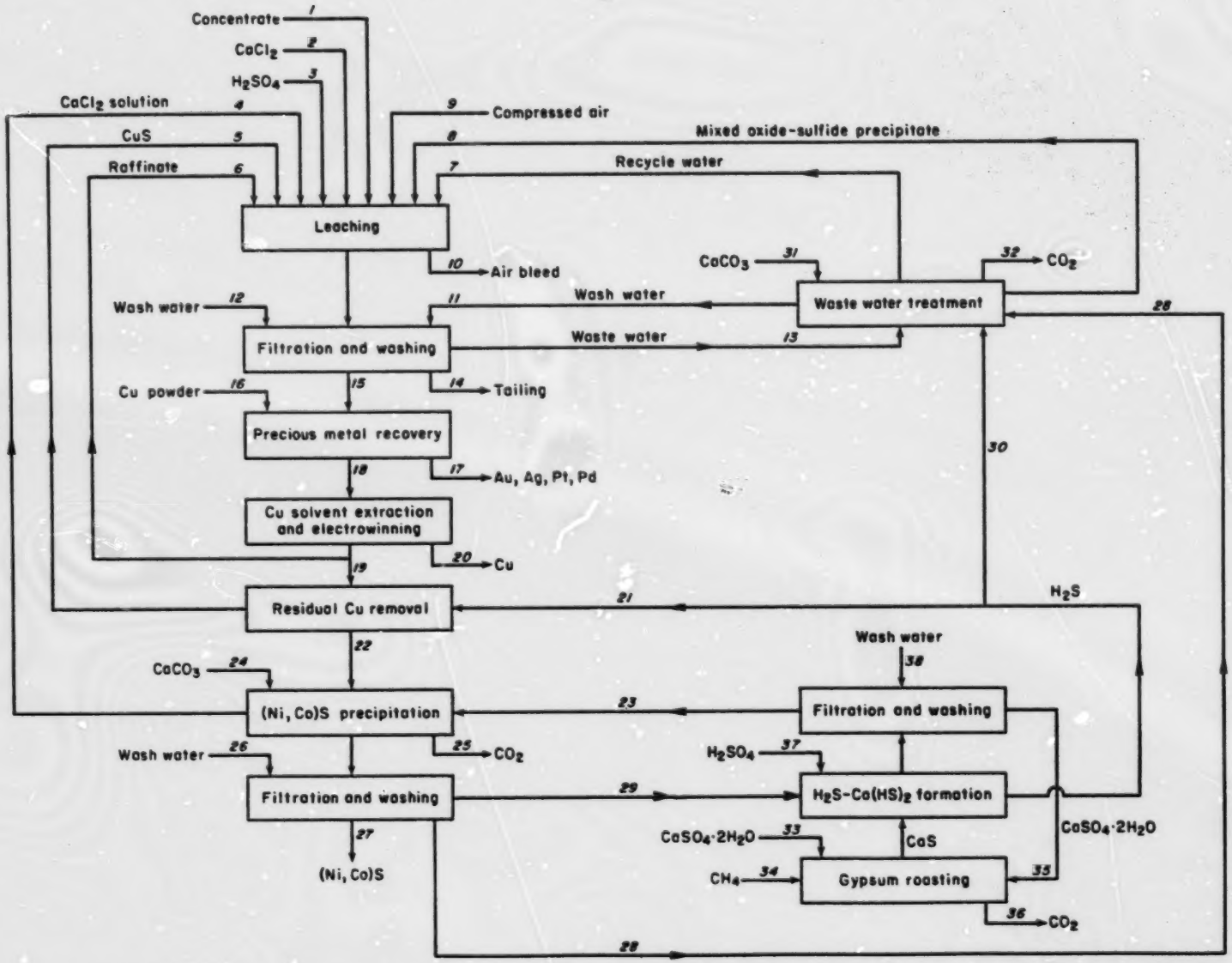

FIGURE 10. - Proposed flowsheet for recovery of copper, cobalt, nickel, and precious metals from a Duluth gabbro flotation concentrate.

TABLE 8. - Partial stream analysis for a 1,000-st/d plant for flowsheet shown in figure 10, short tons per day

Stream	Cu^{2+}	Ni^{2+}	CO^{2+}	Fe^{2+}	Ca^{2+}	Mg^{2+}	SO_4^{2-}	S^{2-}	S	Cl^-	Cu	$CaCO_3$	CO_2	H_2S	CH_4	Air	H_2O	Other	Au[1]	Ag[1]	Pt[1]	Pd[1]	Total
1	93	16	1	280	9	9	16	269	2	-	-	-	-	-	-	-	70	305	13	600	16	34	[2]1,070
2	-	-	-	-	<1	-	-	-	-	1	-	-	-	-	-	-	-	-	-	-	-	-	1
3	-	-	-	-	-	-	44	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	44
4	-	-	-	-	17	2	4	-	-	32	-	-	-	-	-	-	250	-	-	-	-	-	305
5	3	-	-	-	-	-	-	1	-	-	-	-	-	-	-	-	1	-	-	-	-	-	5
6	53	333	19	-	21	37	46	-	-	699	-	-	-	-	-	-	5,960	-	-	-	-	-	7,168
7	-	-	-	-	1	-	-	-	-	3	-	-	-	-	-	-	456	-	-	-	-	-	460
8	14	35	2	-	2	-	4	7	-	-	-	-	-	-	-	-	29	-	-	-	-	-	93
9	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2,500	-	-	-	-	-	-	2,500
10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2,375	-	-	-	-	-	-	2,375
11	-	-	-	-	34	4	1	-	-	70	-	-	-	-	-	-	9,700	-	-	-	-	-	9,809
12	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	235	-	-	-	-	-	235
13	14	35	2	-	2	4	5	-	-	73	-	-	-	-	-	-	10,130	-	-	-	-	-	10,265
14	8	-	-	280	60	9	176	9	232	1	-	-	-	-	-	-	341	254	6	60	10	19	[2]1,370
15	141	349	20	-	22	39	48	-	-	731	-	-	-	-	-	-	6,230	-	7	540	6	15	[2]7,580
16	-	-	-	-	-	-	-	-	-	-	[3]43	-	-	-	-	-	-	-	-	-	-	-	[3]43
17	-	-	-	-	-	-	-	-	-	-	[3]29	-	-	-	-	-	-	-	7	540	6	15	[2,3]68
18	141	349	20	-	22	39	48	-	-	731	-	-	-	-	-	-	6,230	-	-	-	-	-	7,580
19	3	16	1	-	1	2	2	-	-	32	-	-	-	-	-	-	270	-	-	-	-	-	327
20	-	-	-	-	-	-	-	-	-	-	85	-	-	-	-	-	-	-	-	-	-	-	85
21	-	-	-	-	<1	-	-	-	-	-	-	-	-	1	-	-	-	-	-	-	-	-	1
22	-	16	1	-	1	2	2	-	-	32	-	-	-	-	-	-	269	-	-	-	-	-	323
23	-	-	-	-	6	-	-	9	-	7	-	-	-	-	-	-	30	-	-	-	-	-	52
24	-	-	-	-	-	-	-	-	-	-	-	34	-	-	-	-	-	-	-	-	-	-	34
25	-	-	-	-	-	-	-	-	-	-	-	-	15	-	-	-	-	-	-	-	-	-	15
26	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	51	-	-	-	-	-	51
27	-	16	1	-	-	-	4	8	-	-	-	-	-	-	-	-	9	-	-	-	-	-	38
28	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	41	-	-	-	-	-	41
29	-	-	-	-	4	-	-	-	-	7	-	-	-	-	-	-	50	-	-	-	-	-	61
30	-	-	-	-	-	-	-	-	-	-	-	-	-	7	-	-	-	-	-	-	-	-	7
31	-	-	-	-	-	-	-	-	-	-	-	87	-	-	-	-	-	-	-	-	-	-	87
32	-	-	-	-	-	-	-	-	-	-	-	-	38	-	-	-	-	-	-	-	-	-	38
33	-	-	-	-	2	-	5	-	-	-	-	-	-	-	-	-	2	-	-	-	-	-	9
34	-	-	-	-	-	-	-	-	-	-	-	-	-	-	8	-	-	-	-	-	-	-	8
35	-	-	-	-	18	-	43	-	-	-	-	-	-	-	-	-	25	-	-	-	-	-	86
36	-	-	-	-	-	-	-	-	-	-	-	-	22	-	-	-	45	-	-	-	-	-	67
37	-	-	-	-	-	-	44	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	44
38	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	5	-	-	-	-	-	5

- Denotes zero. [1]Troy ounce per day. [2]Includes precious metals. [3]Pound per day.

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SUMMARY AND CONCLUSIONS

A $HCl-O_2$ leaching procedure was demonstrated for treating Duluth gabbro bulk flotation concentrate. A conceptual flow diagram is proposed. The process extracted 90 to 92 pct of the Cu, 99 pct of the Ni, and 97 to 99 pct of the Co under these conditions: 15 pct pulp solids, temperatures from 105° to 120° C, and pressurized to 50 psig with O_2. Very little Fe (<0.1 g/L) remained in the liquor. Precious metal extractions were erratic and unpredictable; a best estimate for their extractions is, in percent, 55 Au, 90 Ag, 40 Pt, and 45 Pd.

Leaching was also conducted with compressed air, which was less costly than using O_2. Powdered Cu was used to cement PM's from solution. Copper was recovered by liquid-liquid extraction and electrowinning. Precipitation of Ni and Co as sulfides produced a $CaCl_2$ solution suitable for recycle to the reactor.

Additional research aimed at improving the leach slurry filtration rate would significantly decrease capital costs, and an improved extractant for Cu from Cl^- solutions would allow better Cu recovery from the pregnant solution.

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